Proceedings of
The 5th Sriwijaya International Seminar on Energy and Environmental Science & Technology
Palembang, Indonesia
September 10-11, 2014

Deacidification of Fatty Oils using Anion Exchange Resin

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ABSTRACT

Crude fatty oils contain a large number of impurities, including gum, free fatty acids, and coloring substances that must be removed in order to create an acceptables refined oil. This paper describes method to deacidify three fatty oils by adsorbing their free fatty acid contents on Rohm and Haas Amberlite IRA 900 anion exchange resin in a fixed bed adsorber. After deacidification, their acid values are lower than 0.6 and the color are brighter. By combining the three steps regeneration method, the resin can be re-utilized without losing its adsorption capacity for 3 cycles.

Keyword: Free fatty acid, deacidification, anion exchange

1. INTRODUCTION

Biodiesel production in Indonesia is mainly based on crude palm oil and produced through transesterification of the oil with methanol in the presence of an alkaline catalyst. As palm oil is edible, some non-edible oils such as Kapok seed oil (*Cieba petandra*), Bagilumbang (*Aleurites trisperma*), Candle nut oil (*Aleurites Moluccana*) are considered as potential alternative raw material for biodiesel production.

Crude fatty oils contain a large number of impurities that must be removed in order to produce acceptable refined oil, particularly for pure plant oil purpose. These impurities generally classified as gum, free fatty acids (FFA), and coloring substances. The FFA content varies among different lipid sources and also depends on the treatments and storage conditions. Some of crude fatty oils such as Bagilumbang seed oil that was produced more than 15 days after the seeds are collected have acid value higher than 10 mg KOH/g. Fatty acids are contained in oils in their free form as a result of the spontaneous lipolysis of the starting triglycerides molecules [8].

When a fatty oil with high FFA content is transesterified, the FFA reacts with the alkali catalyst to form soap. The soap contaminates the fuel by dispersing the micelles of the byproduct glycerine and lowers the fuel yield by interfering phase separation of the fuel and glycerine. To overcome this problem, the feedstock should be preprocessed by deacidification prior to transesterification.

The common methods to remove FFA are washing with alkali, treatment with alumina, distillation under vacuum [1], solvent extraction method or hydrolization method [8]. Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is energy intensive. Moreover, heating oil to high temperature under reduced pressure generates secondary reactions that alter their physicochemical characteristics and organoleptic properties [2]. Pretreatment with alkali prior to membrane filtration resulted in a very high reduction (ca. 90%) of FFA in the processed oils [2]. These approaches, however, lead to high refining loss when applied to high-FFA oils.

Recent work has focus on the use of ion exchange resin as adsorbent for removing the FFA content and also as catalyst for transesterification and esterification of several different raw oils [1, 3-7] in a fixed bed reactor or a continuous stirred reactor. Cation exchange resin catalyst for esterification of the FFA and anion-exchange resin catalyst for transesterification of the triglyceride. Some of the resin that have been investigated are anionic Diaion PA306S and cationic Diaion PK208LH [3, 5], anionic Amberlite A26 and A27 and

cationic Amberlite 15 [4], Lewatit MP500A and MP600 [1], acidic ion-exchange resin EBD-100, EBD-200 and EBD-300 [6], Amberlite A15d (A15) and A46w (A46) [7]. Various triglycerides and diglycerides in the crude oil can be converted to fatty acid methyl ester by transesterification using the anion-exchange resin catalyst; the remaining FFA in the solution can be removed by adsorption on same anion-exchange resin [3]. Not only the FFA but also the water contained in the feed oil was removed from the effluent by the adsorption on the anion-exchange resin [5]. The anion-exchange resin with a lower cross-linking density and a smaller particle size gave a high reaction rate and high conversion [4].

The aim of this work was to decrease the acid value from three different fatty oils with high FFA content by deacidification of fatty oils using a fixed bed column of Rohm and Haas Amberlite IRA 900 anion exchange resin.

2. METHODS

Materials

Kapok seed oil (KSO) with an acid value of about 18 mg KOH/g (obtained from a producer in Semarang, Indonesia), Bagilumbang seed oil (BSO) with an acid value around 13 mg KOH/g (PT. Dharma Prima Mandala, Bandung), Candle nut oil (CNO) with an acid value of about 10 mg KOH/g (pressed in our own laboratory) and technical grade hexane and methanol (Bratachem) were used. An anion exchange resin Amberlite IRA 900 (Rohm and Haas) was used as the active resin. The resin was supplied in the chloride form and therefore, before the experiment, was activated by rinsing it with sodium hydroxide solution (3%) to displace the chloride ion with a hydroxyl ion.

Deacidification experiment

Deacidification was performed using a column packed with resin. The resin volume was 1 liter and the temperature was kept constant at room temperature. The resin was activated by washing it two times, first with 2 bed volume of sodium hydroxide 3% at 50^{o}C and at flow rate of 1 L/hr. This washing is to displace the chloride ion with a hydroxyl ion. Then the resin was washed with 2 bed volume of water at flow rate of 1 L/hr to eliminate the remaining sodium hydroxide.

The mixed feed solution of the fatty oil and n-hexane (1:1) was supplied to the top of the column at the constant flow rate of 0.8 L/hr. Figure 1 shows a schematic diagram of the fatty oil deacidification system. The deacidified fatty oil was then separated from the n-hexane by distillation process. The acid value of fatty oils was measured by the Wijs method. After deacidification process, the resin was rinsed with methanol to eliminate the FFA. The resin was regenerated by the same method proposed for the activation.

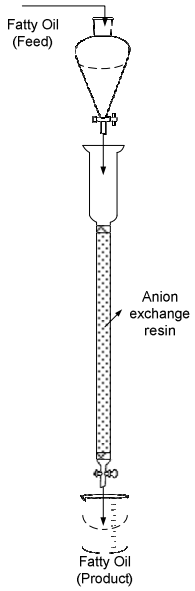

Fig. 1 Schematic diagram of the fatty oil deacidification system

The three fatty oils were very viscous, so n-hexane was used to dissolve the oils and decrease their viscosity. The lower viscosity resulted in good contact between fatty oils and the resin, making the deacidification process functioned well. N-hexane regenerated by distillation process and could be used for the subsequent deacidification.

3. RESULTS

Table 1 lists the results of deacidification with the anionic resin. The process successfully decreased the acid value (AV) of all fatty oil to 0.5. The FFA was bound to the hydroxyl ion of the resin, and then removed by rinsed the resin with methanol.

After regeneration, the resin still yielded low AV oils for the next three cycles. The fourth cycle indicated that the resin was already deactivated, so the AV cannot be decrease to 0.5,

while the fifth cycle result showed the worst value (10.32). Table 2 lists the result of 5 cycles BSO deacidification process. The resin might become deactivated because regeneration flow was done co-currently with deacidification flow, so the residual FFA inhibited the next adsorption process. Backwash regeneration would be more effective.

Table 1 Results of Deacidification in Fixed-Bed Reactor with OH^- Form of Resin

Fatty Oil	AV before process	AV after process	Yield[1]
KSO	18.12	0.59	96.74
BSO	13.20	0.56	95.76
CNO	10.80	0.54	95.00

[1]The yield represents the efficiency of the deacidification and was calculated as: Yield = 100 −(final AV / initial AV) ×100. AV, acid value.

In addition to residual FFA content, adsorbed color body (pigment) and other impurities are not removed from the resin either by rinsing with methanol or sodium hydroxide solution [9]. Consequently, the capacity of the resin may be gradually reduced to the point where the process is no longer efficient. In such cases the exhausted resin must be treated with a solution of an oxidizing agent which removed the adsorbed impurities and restores the capacity of the resin [9].

Table 2 Results of 5 Cycles BSO Deacidification in Fixed-Bed Reactor with Initial AV 13.20

Cycle	Final AV	Yield
1	0.56	95.76
2	0.59	95.53
3	0.59	95.53
4	5.60	57.58
5	10.32	21.82

Photographs of the feed and effluent solutions are shown in figure 2. The effluent solution was transparent yellow single phase, thus the dark brown pigment in the feed oil (KSO) did not flow out. This meant that the pigment was adsorbed on the anion-exchange resin (Amberlite IRA 900) during the progress of the deacidification.

(a) **(b)**

Figure 2 Photographs of (a) feed (KSO) and (b) effluent (KSO) from the column packed with the resin

4. CONCLUSION

Deacidification process can be performed efficiently in a column packed with resin (amberlite IRA 900) as the adsorbent. This process could decreased the acid value to 0.5 and also adsorb the oils pigment. Regeneration with excess methanol or a solution of oxidizing agent might be needed to overcome the saturated resin problem.

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